

PRODUCTION OF SYNTHETIC FUELS FROM COAL BY
HYDROGENATION UNDER MEDIUM PRESSURES

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Abstract

The results of a two stage process for the conversion of a high volatile bituminous coal from Utah to gasoline, diesel oil, gas, and char are described. In the first stage, coal was hydrogenated in a bench scale reactor at high temperatures and medium pressures to get a heavy oil as the main product which was hydrocracked in a subsequent bench scale operation to produce gasoline and diesel oil. The overall material balance indicated that coal can be converted to 30% high octane gasoline, 5% high speed diesel oil, 35% high B.T.U. gas, and 30% char. A conceptual scheme for the processing of 100 tons of coal is proposed.

Introduction

High pressure hydrogenation of coal for the production of synthetic liquid fuels was practised in Germany during World War II. Hydrogenation was carried out at pressures from 5000 to 10,000 psi and the processes were found economically uncompetitive (Gordon, 1947). A demonstration plant for coal hydrogenation at 7500 to 10,000 psi pressure was operated by the U. S. Bureau of Mines during 1949 to 1953 for an economic evaluation of the process (U. S. Bureau of Mines, 1962). The process was found to be economically unfavorable. The technology developed during the last decade indicated the economic feasibility of hydrogenation of coal under medium pressure conditions. The H-coal process was developed for coal hydrogenation under medium pressures of 1500 to 3000 psi and it was operated in an ebullated bed reactor. The pilot plant data demonstrated the economic feasibility of the H-coal process (Alpert, et al., 1964). In the present communication, the results of a two stage hydrogenation process for the conversion of coal to gasoline, diesel oil, gas, and char under medium pressure conditions, are reported.

Experimental

Materials.

A high volatile bituminous A-seam, King Mine, Spring Canyon coal from Utah and high temperature coke (Table 1) were used for

hydrogenation. Analar grade stannous chloride was used as the catalyst. The catalyst was completely soluble in water and insoluble in benzene.

Equipment.

The flow sheet of the bench scale unit for coal hydrogenation is shown in Figure 1. Hydrogen was drawn from the cylinder 1, compressed by the compressor 4, and stored in the storage tank 5. Hydrogen from the storage tank was preheated to about 300°C before it entered the reactor 9. The coal was fed continuously to the reactor from the hopper 7, by a horizontal screw feeder 9, operated by a motor 8. The coal feed rate was controlled by a calibrated device attached to the motor. The reactor was made of 316 stainless steel and was 4 feet high and 2 inches inside diameter. It was provided with a thermowell extending to the center for temperature measurements and lines for the injection of cold hydrogen. Coal gets hydrogenated while it falls down the reactor. The solid and liquid products were collected in the liner of the quench tank 11. The gases passed through the condenser 12 and the condensed liquid was collected in the trap 13. The uncondensed gas was metered by the wet gas meter 14 and let out into the atmosphere. No recycling of the exit gas was practised. The hydrogen flow rate was controlled manually by the high pressure regulating valves 2A-2F. The whole system was designed for a maximum working pressure of 5000 psi at room temperature and the reactor and preheater for 5000 psi at 700°C.

The heavy oil obtained by coal hydrogenation was refined in a continuous bench scale unit with a static bed reactor shown in Figure 2. It consisted of a vertical tubular stainless steel reactor of 0.75-inch inside diameter and 40-inch length with extensive means for controlling temperature, pressure, and gas and liquid flow rates. The first 20 inches of the reactor length from the top was packed with ceramic beads of 0.17-inch diameter, the next 6.5 inches with the catalyst (60 c.c), and the following 12 inches again with ceramic beads. The top bed of ceramic beads acts as the preheating zone. The temperature at the center of the catalyst bed was measured with a thermocouple placed between the reactor and furnace walls. The hydrogen supply was taken from a hydrogen cylinder with a maximum pressure of 2300 psi.

Procedure for coal hydrogenation.

Coal was ground in a hammer mill, screened, and dried at 110°C. The dry coal was impregnated with the catalyst by spraying a water solution of the latter in a mixer. The impregnated coal was again dried to remove all the water. The dry impregnated coal was mixed with an equal quantity of high temperature coke of the same size. About 10 pounds of the coal-coke mixture was charged into the hopper and pressurized with hydrogen. The whole system was first flushed with preheated hydrogen from the storage tank and the

system was pressurized to the desired pressure. The rate of hydrogen flow was maintained at about 15 liters per minute. When the temperature in the reactor was stabilized, coal-coke mixture was fed to the reactor at the rate of about 5 grams per minute. The pressure and temperature inside the reactor were maintained constant throughout. The outlet gas was sampled every half hour for analysis. Each run was carried out for about 15 to 16 hours. After all the coal-coke mixture was fed to the reactor, heating and hydrogen flow were stopped and the system was allowed to cool down to atmospheric temperature. After the system attained atmospheric temperature and pressure, the liner from the quench tank was taken out. The contents of the liner and the light oil trap were weighed. The percentage conversion of coal to gas was calculated from the total quantity of gas passed through the system during each experiment and its analysis. The weight of all the products exceeded the weight of feed and the difference in weight was taken as percent hydrogen consumed in the process. The amount of water formed was found almost equal to the hydrogen consumed and the yield of gaseous, liquid, and solid products was 100% on the basis of coal feed. The oil from the contents of the liner were extracted with benzene and the char separated. The benzene was distilled off to get the oil product. The light oil collected in the trap was added to the oil obtained by benzene extraction to get the total oil product. The char was washed with water to dissolve the catalyst. The resultant char was dried at 110°C and analyzed. The amount of stannous chloride dissolved in the water extract was determined.

Procedure for hydrotreating of oil.

The total oil product obtained from coal was hydrotreated at 420°C, 1500 psi pressure, and a space-velocity of 1.0 over a cobalt-molybdate on alumina industrial catalyst. It was also hydrocracked at 490°C, 2000 psi pressure, and 1.0-space-velocity. The hydrogen consumption in these operations was obtained from the difference in the weight of total products and feed. The liquid product was distilled into different fractions. The light oil fraction boiling up to 200°C was designated as gasoline, the fraction from 200° to 360°C as diesel oil, and the remaining as residue. The diesel oil fraction was refined by extraction with a mixture of dimethyl formamide and n-heptane to improve the diesel index (Qader and Vaidyeswaran, 1966). In the hydrotreating work, the coke deposit inside the reactor was burnt off after each experiment by flushing the reactor at 500°C with air for 10 hours.

Product analysis.

The proximate and ultimate analysis of coal, coke, and char were done by conventional methods. Sulfur was determined by the bomb method and nitrogen by the C-H-N chromatographic analyzer, F. M. Model 185. Hydrocarbon type analysis of the gasoline was done by the Fluorescent-Indicator-Adsorption method (ASTM D-1319-65T). The hydrocarbon types in the heavy oil feed and diesel oil were

determined by chemical methods (ASTM D-1019-62). The naphthenes in the gasoline were estimated by the refractivity intercept method (ASTM D-1840-64). The n-paraffin content was determined by adsorption on 5-A molecular sieves in a glass column of 0.5-inch diameter and 1.5-foot height. The isoparaffins were obtained by the difference. The tar acids and bases were estimated by extraction with 10% sodium hydroxide and 20% sulfuric acid, respectively. The diesel index was calculated from API gravity and aniline point. The octane number was determined by the Research Method. The gas analysis was done by gas chromatography in the F. M. Model 720 dual column programmed temperature gas chromatograph.

Results and Discussion

The admixture of coke with coal in 1:1 ratio eliminated almost all the caking and agglomeration problems in the reactor. No significant conversion of coke was found when it was hydrogenated alone. The presence of coke in the feed did not affect the product distribution to any appreciable extent. The feed particles attained the reaction temperature while they were halfway down the reactor. The coking of the liquid product was minimized due to the short residence time. The hydrogen consumption in the process varied between 4 and 7% of the feed coal and the conversion to water was found to be about 5 to 8%. About 50% of the sulfur and nitrogen in the coal was retained in the char while the remaining was evenly distributed in the liquid and gaseous products. About 70 to 80% of oxygen in the coal was converted to water. About 80% of the catalyst used was recovered by washing the char with water.

The residence time of the feed particles in the reactor was expected to be about 5 seconds and hence the particle size of the feed was of great significance in this work. Coal and coke are bad conductors of heat and need long residence times to get heated to the reaction temperature. Because of the short residence times involved in this process, the size of the coal feed was kept as fine as possible. The influence of the size of feed particles on product distribution is shown in Figure 3. The conversion of coal to liquid and gaseous products decreased with an increase in the particle size while the yield of char increased. A particle size of about 50 microns was found to affect maximum conversion of coal. However, for practical reasons, a particle size of about 250 microns was used in this investigation. A longer reactor might be necessary for feeding larger particles effectively.

A large excess of the catalyst was used in these experiments to bring about adequate contact between the coal particles, catalyst, and hydrogen. Several catalysts were used for coal hydrogenation (Table II) and stannous chloride affected maximum coal conversion of 75% at an optimum concentration of 15% by weight of coal (Figure 4). A part of the stannous chloride might vaporize and decompose during the process and may not take part in the hydrogenation of coal. Only the undecomposed stannous chloride might be catalyzing

the reactions, as also pointed out by Zielke, et al. (1966), necessitating the usage of a large excess of the catalyst. The higher conversions obtained with stannous chloride might probably be due to its known better thermodynamic stability toward decomposition when compared to the other metal halides used.

Temperature and pressure had marked influence on product distribution. The yield of liquid product increased up to 515°C but decreased at higher temperatures while the yield of gas increased linearly with temperature. The yield of char decreased up to 515°C but remained almost the same at higher temperatures (Figure 5). A temperature of 515°C was found to be optimum for maximum liquid product yield. Above 515°C, cracking of the liquid product took place with the production of gas. The liquid product increased with pressure with a corresponding decrease in the yield of char. Pressure had little effect on gas yield (Figure 6). A pressure of 2000 psi was found to be optimum for maximum conversion.

The analysis of the products obtained at 515°C and 2000 psi pressure is given in Table III. The liquid product was somewhat similar to low temperature tar. It was light and contained 20% light oil boiling up to 200°C and 20% tar acids. The composition of the liquid product indicated that considerable cracking of the primary product took place during the process. The gaseous product, exclusive of process hydrogen, contained about 85% methane with small quantities of ethane and propane. The gas composition indicated that it can be used as a substitute for natural gas. The char (Table III) was produced when coal was hydrogenated without mixing with high temperature coke and it was found to be as good as high temperature coke in reducing caking and agglomeration of coal during hydrogenation. It can be used for power generation or hydrogen production.

Hydrotreating of the liquid product at 420°C, 1500 psi pressure, and 1-space-velocity (Table IV) yielded 26% gasoline of 78 research octane and 56% of diesel oil with 43 diesel index. Solvent refining of diesel oil yielded 48% of high speed diesel oil. The hydrocracking of the liquid product over the dual-functional catalyst yielded 69% of gasoline of 93 research octane and 17% of low speed diesel oil. After solvent refining, high speed diesel oil was obtained in a yield of 12% (Table V). The tar acids, sulfur, and nitrogen were removed almost completely during hydrotreating and hydrocracking operations. Hydrogen consumption varied between 2 and 3% of the oil in these operations.

The overall material balance is schematically shown in Figure 7. Scheme I represents the yield of various products from a single charge of 10 pounds containing 5 pounds of coal. The amount of hydrogen consumed in the process was found to be approximately equal to the amount of water formed. Scheme II represents the nature and overall yield of the products from coal. The gas yield in this scheme comprised of the yield of gas in both the operations

in Scheme I. Similarly, the char comprised of the char and residue produced in Scheme I. The conceptual product yields (Table VI) were calculated from the data covering several batch runs. The char produced in the process was used in admixture with coal in 1:1 ratio and the hydrogen consumption in both the stages of the process was approximated to 6% of the coal feed. The material balance in Table VI was obtained by calculating the yields after normalization of the total product recovery to 106 wt. % of coal feed. A conceptual schematic diagram of a coal refinery utilizing the two stage process described in this paper is shown in Figure 8. The results obtained in this investigation demonstrated the technical feasibility of the two stage process for the conversion of coal to high octane gasoline, high speed diesel oil, and high B.T.U. gas.

Acknowledgement

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Table 1. Properties of coal and coke.

	<u>Coal</u>	<u>Coke</u>
Proximate analysis, wt. % (moisture free basis)		
Volatile matter	46.8	2.5
Ash	6.7	10.0
Fixed carbon	46.5	87.5
Ultimate analysis, wt. %		
Carbon	75.88	-
Hydrogen	5.58	-
Oxygen	9.50	-
Sulfur	0.94	-
Nitrogen	1.50	-
Calorific value, BTU/lb	13,250	-

Table II. Product distribution with different catalysts.
 Temperature, 515°C; pressure, 2000 psi

<u>Catalyst</u>	<u>Product distribution, wt. %</u>			
	<u>Total conversion</u>	<u>Oil</u>	<u>Gas</u>	<u>Char</u>
Stannous chloride	75.0	43.0	32.0	25.0
Ammonium molybdate	69.0	39.0	30.0	31.0
Nickel chloride	71.0	41.0	30.0	29.0
Ferrous chloride	65.0	38.0	27.0	35.0
Zinc chloride	55.0	29.0	26.0	45.0

Table III. Properties of products.
 Temperature, 515°C
 Pressure, 2000 psi

Liquid product

Sp. gr, 20°C	0.9946
Sulfur, wt. %	0.3214
Nitrogen, wt. %	0.5820
Tar acids, vol. %	20.0
Tar bases, wt. %	1.50
Distillation data	
I.B.P., °C	75
Up to 200°C, vol. %	20.0
Up to 350°C, vol. %	72.0
Residue, vol. %	28.0
Hydrocarbon types in neutral oil	
up to 350°C, vol. %	
Saturates	46.0
Olefins	6.0
Aromatics	48.0

Gas composition, vol. %

Hydrogen	94.0
Methane	5.0
Ethane	0.5
Propane	0.5

Char analysis, wt. %

Volatile matter	7.0
Ash	12.0
Fixed carbon	81.0
Carbon	77.5
Hydrogen	5.4
Oxygen	2.6
Sulfur	0.38
Nitrogen	0.62
Calorific value, BTU/lb	14,000

Table IV. Yields and quality of hydrotreated products.
 Temperature, 420°C; pressure, 1500 psi; sp.
 vel., 1.0; catalyst, cobalt-molybdate on
 alumina

Yields, vol. %

Total product	99.0
Gasoline	26.0
Diesel oil	56.0
Refined diesel oil	48.0
Gas	2.0
Residue	12.0

Composition of gasoline, vol. %

Saturates	58.0
Olefins	3.0
Aromatics	39.0
Research octane number	78.0
Diesel index of diesel oil	43.0
Diesel index of refined diesel oil	50.0

Table V. Yields and quality of hydrocracked products.
 Temperature, 490°C; pressure, 2000 psi; sp.
 vel., 1.0; catalyst, nickel sulfide-tungsten
 sulfide on silica-alumina

Yields, vol. %

Total product	100.0
Gasoline	69.0
Diesel oil	17.0
Refined diesel oil	12.0
Gas	8.0
Residue	6.0

Composition of gasoline, vol. %

Aromatics	52.0
Isoparaffins	21.0
Olefins	2.0
Naphthenes	8.0
N-paraffins	17.0
Research octane number	93.0
Diesel index of diesel oil	31.0
Diesel index of refined diesel oil	50.0

Table VI. Conceptual product yields.
Coal, 100 tons (m.a.f.)
Hydrogen, 6 tons

<u>Products</u>	<u>Quantities</u>
C ₁ -C ₃ gases, cu. ft.	1,384,930
Gasoline, Bbl.	232
Diesel oil, Bbl.	33
Char, tons	28
Water, gallons	1,670
Hydrogen sulfide, cu. ft.	20,833
Ammonia, tons	1

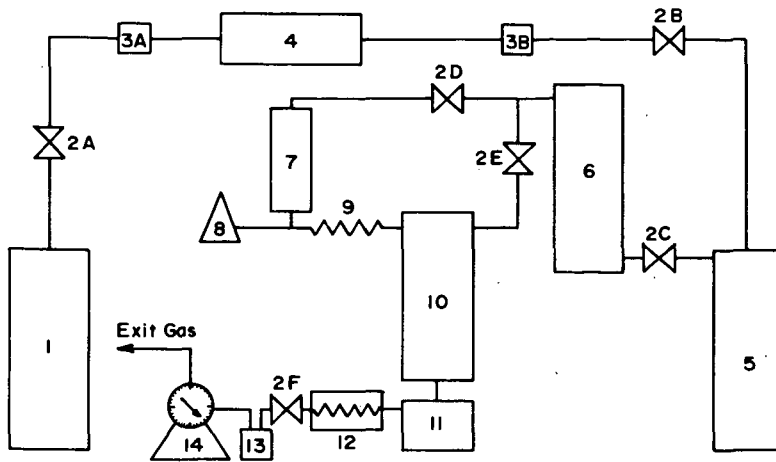


Figure 1. Flow sheet of coal hydrogenation unit.

1. Hydrogen cylinder, 2A-2F. High pressure regulating Valves, 3A & 3B. Filters, 4. Compressor, 5. Storage tank, 6. Preheater, 7. Hopper, 8. Motor, 9. Screw feeder, 10. Reactor, 11. Quench tank, 12. Condenser, 13. Liquid trap, 14. Wet gas meter.

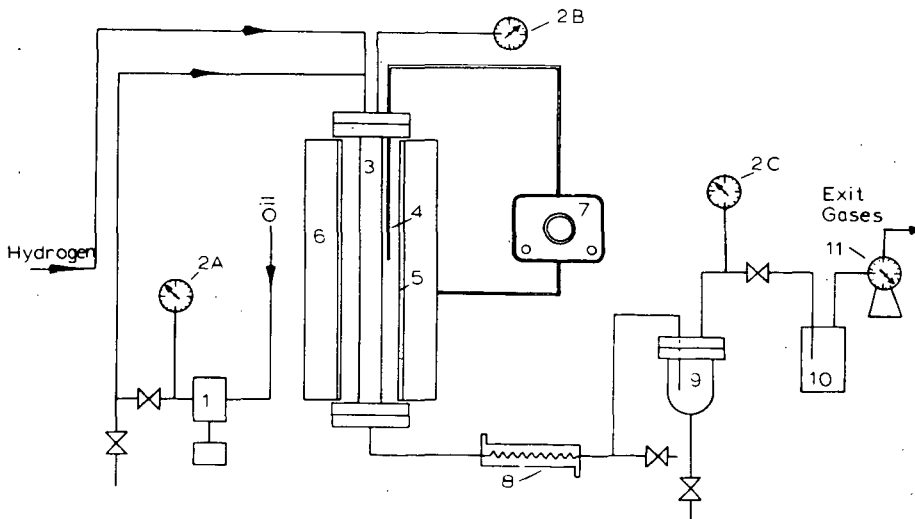


FIGURE 2. FLOW SHEET OF THE HYDROTREATING UNIT.
1. HIGH PRESSURE PUMP, 2A, 2B, 2C. PRESSURE GAUGE, 3. REACTOR, 4. THERMO-
COUPLE, 5. CERAMIC FURNACE, 6. INSULATION, 7. TEMPERATURE CONTROLLER,
8. CONDENSER, 9. SEPARATOR, 10. ACTIVE CARBON TOWER, 11. GAS METER.

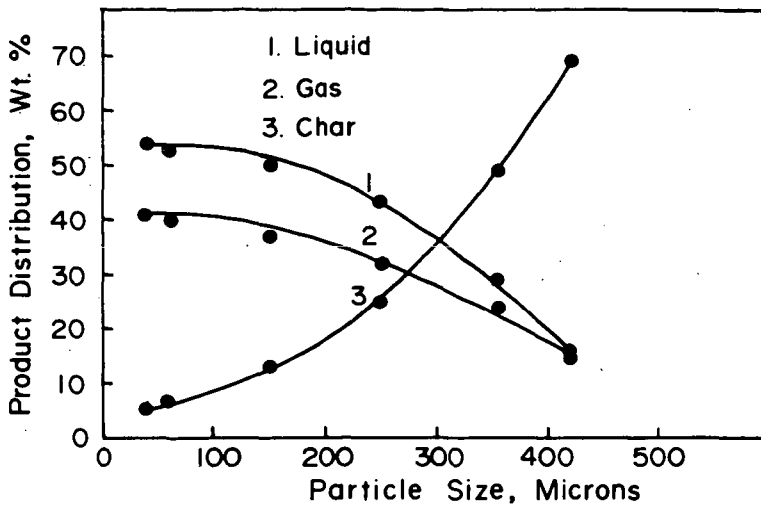


Figure 3. Effect of particle size on product distribution. Pressure, 2000 psi; Catalyst, 15% by weight; Temperature, 515° C.

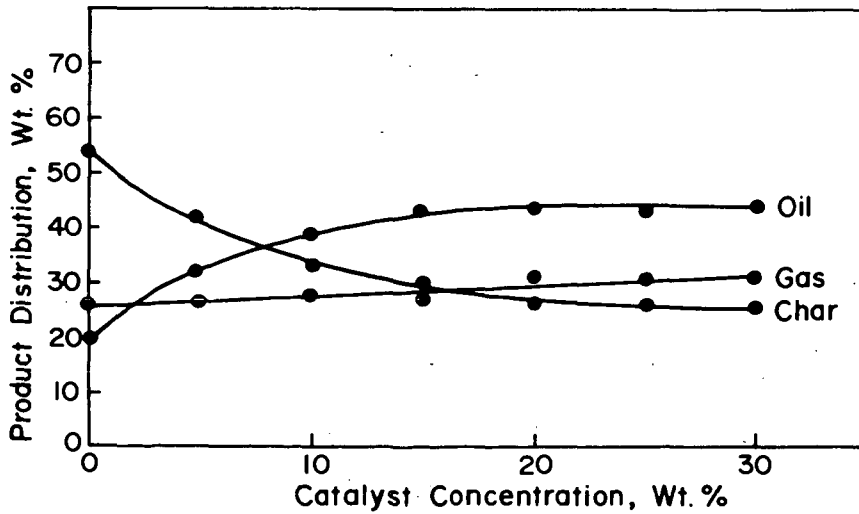


Figure 4. Effect of catalyst concentration on product distribution. Temperature, 515° C.; Pressure, 2000 psi.; Size, 250 microns.

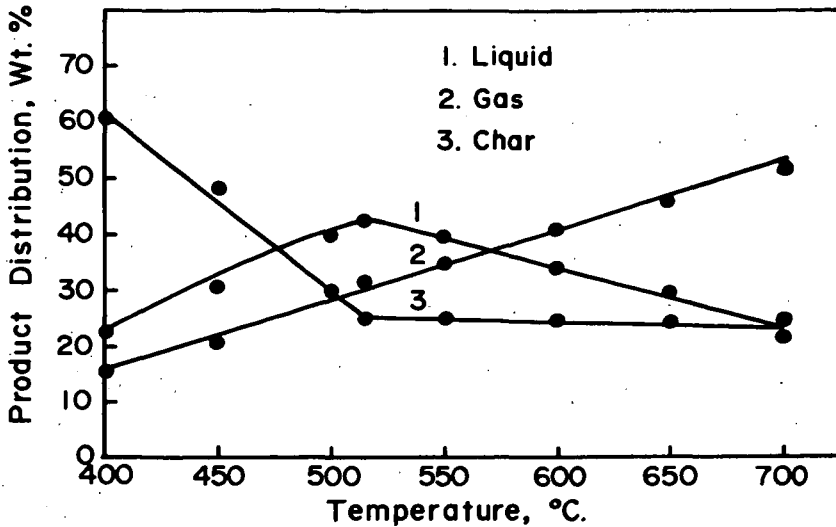


Figure 5. Effect of temperature on product distribution.
Pressure, 2000 psi; Size, 250 microns;
Catalyst, 15% by weight.

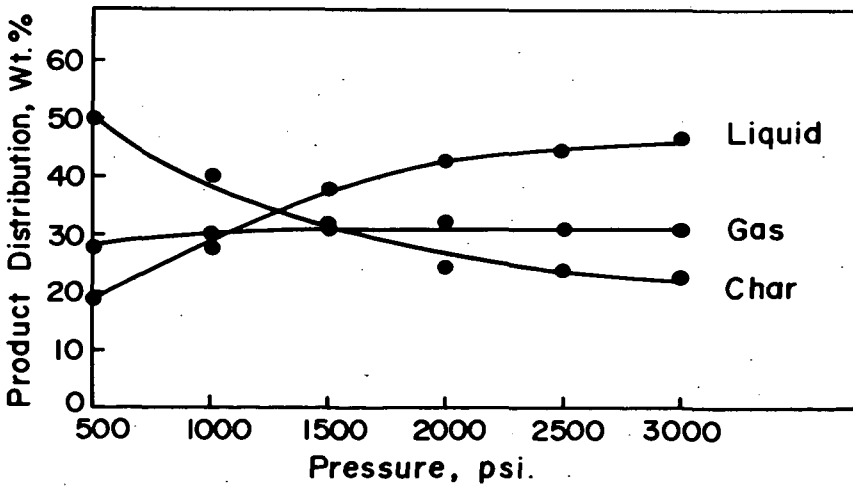


Figure 6. Effect of pressure on product distribution.
Temperature, 515°C.; Size 250 microns;
Catalyst, 15% by weight.

